

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2003-300278

(43)Date of publication of application : 21.10.2003

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(51)Int.Cl. B32B 15/08  
C23C 22/42  
C23C 22/53  
C23C 28/00

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### (54) DECORATIVE STEEL SHEET

#### (57)Abstract:

PROBLEM TO BE SOLVED: To provide a decorative steel sheet obtained by laminating an organic resin film on a plated steel sheet in which a zinc-plated film and a posttreated film not containing chromium are formed and having excellent environmental suitability, and resin adhesive properties and corrosion resistance equivalent to those of the plated steel sheet in which the conventional posttreated film containing the chromium is formed.

SOLUTION: The decorative steel sheet comprises the plated steel sheet in which the zinc-plated film and a posttreated film containing vanadium or cobalt in its upper layer are formed on both surfaces of the steel sheet, and an organic resin film laminated on at least one surface of the plated steel sheet.

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### LEGAL STATUS

[Date of request for examination] 24.06.2004

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or

application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's  
decision of rejection]

[Date of requesting appeal against examiner's  
decision of rejection]

[Date of extinction of right]

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CLAIMS

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[Claim(s)]

[Claim 1] The makeup steel plate which comes to carry out the laminating of the organic resin coat to at least one side of the plating steel plate with which the galvanization coat and the after-treatment coat which contains vanadium in the upper layer were formed in both sides of a steel plate.

[Claim 2] The makeup steel plate which comes to carry out the laminating of the organic resin coat to at least one side of the plating steel plate with which the galvanization coat and the after-treatment coat which contains cobalt in the upper layer were formed in both sides of a steel plate.

[Claim 3] The makeup steel plate according to claim 1 to 2 characterized by said galvanization coat being a composite-coatings coat of zinc, cobalt, and molybdenum.

[Claim 4] The makeup steel plate according to claim 1 to 3 with which a polyacrylic acid spreading coat is further formed in the upper layer of said after-treatment coat, and it comes to carry out the laminating of said organic resin coat on this polyacrylic acid spreading coat.

[Claim 5] 4 is [ \*\*\*\*\* 1 characterized by said organic resin coat coats being any one sort of monolayer coats of one film of polyolefin resin, polyester resin, acrylic resin, and polyvinyl chloride resin, or the coating spreading film, or a multilayer coat which comes to carry out the laminating of the two or more sorts thru/or ] the makeup steel plate of a publication either.

[Claim 6] The makeup steel plate according to claim 1 to 5 characterized by the surface electrical resistance (JIS K 7194) of the plating side of other one side where the laminating of said organic resin coat is carried out only to one side, and the laminating of the organic resin coat is not carried out in a makeup steel plate according to claim 1 to 5 being 0.5ohms or less.

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[Translation done.]

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to the environment-friendly makeup steel plate which does not use chromium for an after-treatment coat at a detail about the makeup steel plate which carried out the laminating of the organic resin coat at the steel plate which makes it come to form an after-treatment coat in a galvanization coat and its upper layer.

[0002]

[Description of the Prior Art] The laminating of the coloring organic resin coat is carried out to a plating steel plate, embossing is performed to a front face or the makeup steel plate which printed the design and raised design nature is suitably used as sheathing covering of electrical machinery products, such as a personal computer, audio equipment, and a refrigerator. Since the makeup steel plate has the endurance which was excellent to the environment of indoor and the outdoors, it is applied also to building-materials applications, such as a wallplate of a modular bath, and an outer wall of a residence. In order that a makeup steel plate may secure the corrosion resistance of the steel plate of a substrate, what carried out the laminating of the organic resin coat to the steel plate with which the galvanization coat was generally formed is used, but in order to raise the adhesive property of an organic resin coat and a galvanization coat, and the corrosion resistance of a galvanization coat, it is common on the front face of a galvanization coat to perform various kinds of chromate treatment, such as an electrolytic chromate treatment, phosphoric-acid chromate treatment, and spreading mold chromate treatment containing hexavalent chromium, as after treatment. However, the spreading mold chromate treatment coat contains harmful hexavalent chromium. Moreover, although the hexavalent chromium with an electrolytic chromate treatment coat harmful in a chromate film does not contain, the demand to the makeup steel plate which is using the chromic-acid solution which is chromium of 6 \*\* in case it manufactures, and does not use hexavalent chromium from a rise of environmental consciousness at the time of manufacture is increasing.

[0003]

[Problem(s) to be Solved by the Invention] This invention aims at offering the makeup steel plate which has a resin adhesive property and corrosion resistance equivalent to the plating steel plate in which the after-treatment coat which is excellent in environmental fitness and contains conventional chromium was formed by carrying out the laminating of the organic resin coat to the plating steel plate in which the galvanization coat and the after-treatment coat which does not contain chromium were formed.

[0004]

[Means for Solving the Problem] The makeup steel plate of this invention at least on one side of the plating steel plate with which the galvanization coat and the after-treatment coat which contains vanadium in the upper layer were formed in both sides of a steel plate At least on one side of the makeup steel plate which comes to carry out the laminating of the organic resin coat, or the plating steel plate with which the galvanization coat and the after-treatment coat which contains cobalt in the upper layer were formed in both sides of a steel plate It is the makeup steel plate which comes to carry out the

laminating of the organic resin coat, and said galvanization coat is a composite-coatings coat of zinc, cobalt, and molybdenum, Moreover, the thing for which it comes to form a polyacrylic acid spreading coat in the upper layer of said after-treatment coat further, Said organic resin coat coat further again Polyolefin resin, polyester resin, It is characterized by being any one sort of monolayer coats of either film of acrylic resin and polyvinyl chloride resin, or the coating spreading film, or the multilayer coat which comes to carry out the laminating of the two or more sorts, and also sets to one of the above-mentioned makeup steel plates. It is characterized by the surface electrical resistance (JIS K 7194) of the plating side of other one side where the laminating of said organic resin coat is carried out only to one side, and the laminating of the organic resin coat is not carried out being 0.5ohms or less.

[0005]

[Embodiment of the Invention] this invention person etc. performs after treatment which consists of various metal plating and organic system processing on a steel plate a galvanization coat and on it. By forming the after-treatment coat after-treatment coat containing vanadium or cobalt in the upper layer of a galvanization coat, as a result of inquiring wholeheartedly about an adhesive property and corrosion resistance with the organic resin coat which carries out a laminating to the formed after-treatment coat and its upper layer It found out that the makeup steel plate which is excellent in an adhesive property and corrosion resistance with an organic resin coat could be manufactured.

[0006] The plating steel plate used for the makeup steel plate of this invention makes a galvanization coat form in both sides of a steel plate, and makes an after-treatment coat form on it. Board thickness currently generally manufactured as a steel plate: Apply 0.1-2mm cold rolled sheet steel. As a galvanization made to form on a steel plate, electrolytic zinc plating, the compound electrolysis plating of zinc, cobalt, and molybdenum, hot dip zincing, melting aluminum zinc alloy plating, zinc-nickel alloy plating, etc. can be used. Especially the steel plate that performed compound electrolysis plating of zinc, cobalt, and molybdenum is suitable for adhesive improvement with corrosion resistance and an organic resin coat. The amount of coats of these galvanization coats is chosen in the range of 1 - 100 g/m<sup>2</sup> as zinc per one side by the application.

[0007] The after-treatment coat which contains vanadium or cobalt in the upper layer of the above-mentioned galvanization coat is made to form in the makeup steel plate of this invention. The after-treatment coat which contains vanadium first is explained. Although the coat containing vanadium mainly consists of banazin san ghosts, it can raise corrosion resistance further by making Lynn contain in a coat. Especially the amount of coats of vanadium is 5 mg/m<sup>2</sup> per one side from an adhesive property with various kinds of organic resin coats which carry out a postscript although not limited, and a corrosion resistance viewpoint. The above is needed. Although corrosion resistance improves with the increment in the amount of coats, it is 1000mg/m<sup>2</sup>. Even if it exceeds, the corrosion resistance improvement effectiveness is saturated, and in the amount of coats beyond it, it becomes disadvantageous economically. therefore, the range of the desirable amount of coats -- 5 - 1000 mg/m<sup>2</sup> it is -- the range of 10 - 500 mg/m<sup>2</sup> is more desirable. About the content of Lynn in a coat, it is an adhesive property with various organic resin coats, and a corrosion resistance viewpoint to per [ 5 ] one side - 1000 mg/m<sup>2</sup>. It is desirable that it is the range. Moreover, as an amount of coats of the vanadium from which good conductivity is acquired although it is applicable only in respect of the galvanization with which one side has not covered the organic resin coat when using a makeup steel plate for the application which needs conductivity, they are 200 mg/m<sup>2</sup>. It is desirable that it is the following.

[0008] The after-treatment coat containing vanadium can be made to form not only with an electrolytic decomposition process but with a non-electrolytic decomposition process. As a non-electrolytic decomposition process, dip coating, the after [ immersion ] roll extracting method, the roll coat method, etc. are applicable. Elements other than vanadium, such as molybdenum, titanium, a zirconium, aluminum, magnesium, and Lynn, may be made to exist in coincidence in a coat for the purpose of corrosion-resistant improvement. Although not restricted especially concerning the vanadium compound used for processing liquid, it is desirable the vanadium fluoride which is generally easy to come to hand, vanadium chloride, a vanadium oxide, a 2 chlorination vanadium oxide, and to use any one sort, such as a vanadium oxide and oxidization vanadium sulfate, or two sorts or more 2 bromination. The total

amount of the content of these vanadium compounds in processing liquid is 5 - 50 g/L preferably three to 150 g/L. In the case of less than 3 g/L, there are few amounts of generation of a coat, and a good coat property is not acquired. If 150 g/L is exceeded, it will be easy to generate an irregular color in a coat, and the processing adhesion of a coat will fall. In addition to a chemical being still more expensive, the amount carried out by adhering to a steel plate at the time of processing increases, and it becomes less economical.

[0009] As a pH regulator of processing liquid, any one sort of the phosphorus compounds, such as a phosphoric acid, phosphate, a polyphosphate, and heavy phosphate, or two sorts or more are used. As heavy phosphate, heavy ammonium phosphate, heavy sodium phosphate, heavy calcium phosphate, heavy magnesium phosphate, and heavy aluminium phosphate are contained. These phosphorus compounds not only act as a pH regulator, but have the effectiveness of raising rust-proofing nature, by incorporating Lynn in a processing coat. The content in the processing liquid in the case of using these phosphorus compounds as a pH regulator is 5 - 50 g/L preferably three to 150 g/L. In the case of less than 3 g/L, there are few amounts of generation of a coat, and a good coat property is not acquired. If 150 g/L is exceeded, the processing adhesion of a coat will fall. The amount furthermore carried out by adhering to a steel plate at the time of processing increases, and it becomes less economical.

[0010] As for pH of processing liquid, it is desirable that it is in one to 6 range, and it is more desirable that it is in the range of 2-4. When pH is less than one, the deposit effectiveness of a coat falls, and the coat of sufficient thickness is hard to be obtained. On the other hand, if pH exceeds 6, processing liquid becomes unstable and does not fit practical use. Even if pH of processing liquid adds acid, such as alkaline substances, such as aqueous ammonia, a sodium hydroxide, and a sodium carbonate, and/or a hydrochloric acid, a sulfuric acid, and a nitric acid, it can be adjusted, but in order to improve a coat property, it is effective to use the above-mentioned phosphorus compounds, such as phosphate. As for the temperature of processing liquid, it is desirable that it is the range of 20-50 degrees C.

[0011] any one sort of a further water-soluble molybdenum compound in order to improve stain resistance in the above-mentioned processing liquid, a titanium compound, a zirconium compound, an aluminium compound, and the magnesium compound -- or two or more sorts may add. As these compounds, oxy-sulfuric-acid molybdenum, sulfuric-acid titanyl, zirconium sulfate, an ammonium molybdate, titanate-acid ammonium, magnesium sulfate and the heavy magnesium phosphate that is the above-mentioned phosphorus compounds, heavy aluminium phosphate, etc. are contained. the content in processing liquid -- any one sort of the aforementioned vanadium compounds, these molybdenum compounds, a titanium compound, a zirconium compound, an aluminium compound, and the magnesium compound, or two sorts or more of total amounts -- it is -- 3-150g/L -- it is 5 - 50 g/L preferably. In the case of less than 3 g/L, there are few amounts of generation of a coat, and a good coat property is not acquired. If 150 g/L is exceeded, it will be easy to generate an irregular color in a coat, and the processing adhesion of a coat will fall. In addition to a chemical being still more expensive, the amount carried out by adhering to a steel plate at the time of processing increases, and it becomes less economical. The stain resistance of a coat is improved by incorporating the matter originating in the molybdenum compound added during these baths, a titanium compound, a zirconium compound, an aluminium compound, a magnesium compound, etc. in the after-treatment coat containing vanadium. Furthermore, in order to raise the electric conductivity of a coat and to stabilize processing liquid, 50 or less g/L of salts, such as a sodium sulfate, an ammonium sulfate, and an ammonium chloride, may be made to contain.

[0012] An after-treatment coat is made to generate on a galvanized steel sheet using the processing liquid created as mentioned above. When using immersion processing as a non-electrolytic decomposition process, the after-treatment coat of sufficient thickness is obtained in a galvanized steel sheet by being preferably immersed for 2 to 10 seconds for 1 to 60 seconds into processing liquid. Even if immersed 60 seconds or more, the thickness of a coat will not increase so much. When using an electrolysis approach, a thick coat is obtained by cathode electrolysis for a short time, and it is 0.5 - 100 A/dm<sup>2</sup>. Processing with current density is desirable. In less than two 0.5 A/dm<sup>2</sup>, the growth of anodic oxide film takes time amount too much, and a thick coat cannot be obtained in a short time. In the case

of pH6 which is the high pH side in an acid field although influenced of pH of processing liquid, current density is 100 A/dm<sup>2</sup>. If it exceeds, YAKE will be produced and a uniform coat will not be obtained. Moreover, if a processing coat becomes thick, processing adhesion will fall.

[0013] Thus, adhesion with the galvanized steel sheet and the organic resin coat in which the after-treatment coat obtained was made to form applies the adhesives suitable for each organic resin coat to an after-treatment coat, in contact with a it top, pressurizes an organic resin coat, and sticks by pressure and carries out a laminating. In order to raise further the adhesive property of an after-treatment coat and an organic resin coat, it found out that it was desirable on an after-treatment coat to apply organic resin and silane coupling agents, such as polyacrylic acid, urethane resin, and acrylic resin, and especially polyacrylic acid was suitable for it. Although especially the coverage of polyacrylic acid is not limited, it is little, and when it is effective and economical efficiency is taken into consideration, it is desirable that it is 0.5 - 1000 mg/m<sup>2</sup> in the amount of coats, and it is more desirable that it is 1 - 500 mg/m<sup>2</sup>.

[0014] Next, the after-treatment coat containing cobalt is explained. The coat containing cobalt consists of metal cobalt and cobalt oxide. Although especially the amount of coats of the after-treatment coat containing cobalt is not limited, it needs two or more one side 1 mg/m from an adhesive property with various organic resin coats, and a corrosion resistance viewpoint, and although corrosion resistance improves with the increment in the amount of coats, even if the amount of coats exceeds 1000 mg/m<sup>2</sup>, corrosion resistance does not improve greatly. Then, when economical efficiency is taken into consideration, as for the amount of coats of cobalt, it is desirable that it is 3 - 1000 mg/m<sup>2</sup>, and it is more desirable that it is 5 - 500 mg/m<sup>2</sup>. Moreover, when used for the application which needs the conductivity of the after-treatment coat on the galvanization coat by which one side is not covered with an organic resin coat, it is the amount of coats 400 mg/m<sup>2</sup> Good conductivity is acquired by considering as the following.

[0015] The after-treatment coat containing cobalt can be made to form not only with an electrolytic decomposition process but with a non-electrolytic decomposition process. As a non-electrolytic decomposition process, dip coating, the after [ immersion ] roll extracting method, the roll coat method, etc. are applicable. Elements other than cobalt, such as vanadium, molybdenum, titanium, a zirconium, aluminum, magnesium, and Lynn, may be made to exist in coincidence in a coat for the purpose of corrosion-resistant improvement. Although not restricted especially concerning the cobalt compound used for processing liquid, it is desirable to use any one sort, such as cobalt sulfate which is generally easy to come to hand, cobalt fluoride, a cobalt chloride, and cobalt oxide, or two sorts or more. The total amount of the content in the processing liquid of these cobalt compounds is 5 - 50 g/L preferably three to 150 g/L. In the case of less than 3 g/L, there are few amounts of generation of a coat, and a good coat property is not acquired. If 150 g/L is exceeded, it will be easy to generate an irregular color in a coat, and the processing adhesion of a coat will fall. In addition to a chemical being still more expensive, the amount carried out by adhering to a steel plate at the time of processing increases, and it becomes less economical.

[0016] As for pH of processing liquid, it is desirable that it is 1-6, and it is more desirable that it is 2-4. When pH is less than one, the deposit effectiveness of a coat falls, and the coat of sufficient thickness is hard to be obtained. When pH exceeds 6, processing liquid becomes unstable and stops on the other hand, fitting practical use. Even if pH of processing liquid adds acid, such as alkaline substances, such as aqueous ammonia, a sodium hydroxide, and a sodium carbonate, and/or a hydrochloric acid, a sulfuric acid, and a nitric acid, it can be adjusted.

[0017] any one sort of a further water-soluble molybdenum compound in order to improve stain resistance in the above-mentioned processing liquid, a titanium compound, a zirconium compound, an aluminium compound, and the magnesium compound -- or two or more sorts may add. As these compounds, oxy-sulfuric-acid molybdenum, sulfuric-acid titanyl, zirconium sulfate, an ammonium molybdate, titanic-acid ammonium, magnesium sulfate and the heavy magnesium phosphate that is phosphorus compounds, heavy aluminium phosphate, etc. are contained. the content in processing liquid -- any one sort of the aforementioned cobalt compounds, these molybdenum compounds, a titanium compound, a zirconium compound, an aluminium compound, and the magnesium compound, or two

sorts or more of total amounts -- it is -- 3-150g/L -- they are 5-50g/L preferably. In the case of less than 3 g/L, there are few amounts of generation of a coat, and a good coat property is not acquired. If 150 g/L is exceeded, it will be easy to generate an irregular color in a coat, and the processing adhesion of a coat will fall. In addition to a chemical being still more expensive, the amount carried out by adhering to a steel plate at the time of processing increases, and it becomes less economical. The stain resistance of a coat is improved by incorporating the matter originating in the molybdenum compound added during these baths, a titanium compound, a zirconium compound, an aluminium compound, a magnesium compound, etc. in the after-treatment coat containing cobalt. Furthermore, in order to raise the electric conductivity of a coat and to stabilize processing liquid, 50 or less g/L of salts, such as a sodium sulfate, an ammonium sulfate, and an ammonium chloride, may be made to contain.

[0018] An after-treatment coat is made to generate on a galvanized steel sheet using the processing liquid created as mentioned above. When using immersion processing as a non-electrolytic decomposition process, the after-treatment coat of sufficient thickness is obtained in a galvanized steel sheet by being preferably immersed for 2 to 10 seconds for 1 to 60 seconds into processing liquid. Even if immersed 60 seconds or more, the thickness of a coat will not increase so much. When using an electrolysis approach, a thick coat is obtained by cathode electrolysis for a short time, and it is 0.5 - 100 A/dm<sup>2</sup>. Processing with current density is desirable. In less than two 0.5 A/dm<sup>2</sup>, the growth of anodic oxide film takes time amount too much, and a thick coat cannot be obtained in a short time. In the case of pH6 which is the high pH side in an acid field although influenced of pH of processing liquid, current density is 100 A/dm<sup>2</sup>. If it exceeds, YAKE will be produced and a uniform coat will not be obtained. Moreover, if a processing coat becomes thick, processing adhesion will fall.

[0019] Thus, adhesion with the galvanized steel sheet and the organic resin coat in which the after-treatment coat obtained was made to form applies the adhesives suitable for each organic resin coat to an after-treatment coat, in contact with a it top, pressurizes an organic resin coat, and sticks by pressure and carries out a laminating. In order to raise further the adhesive property of an after-treatment coat and an organic resin coat, it found out that it was desirable on an after-treatment coat to apply organic resin and silane coupling agents, such as polyacrylic acid, urethane resin, and acrylic resin, and especially polyacrylic acid was suitable for it. Although especially the coverage of polyacrylic acid is not limited, it is little, and when it is effective and economical efficiency is taken into consideration, it is desirable that it is 0.5 - 1000 mg/m<sup>2</sup> in the amount of coats, and it is more desirable that it is 1 - 500 mg/m<sup>2</sup>.

[0020] After making an after-treatment coat form further on the plating steel plate in which the galvanization coat was made to form as mentioned above, the laminating of the organic resin coat is carried out, and it considers as the makeup steel plate of this invention. 5-300 micrometers is suitable for the thickness of an organic resin coat. Things can be carried out using the organic resin coat more than one layer chosen from the spreading film of common coatings, such as the film which consists of thermoplastics, such as acrylic resin, such as polyolefin resin, such as polyethylene, polypropylene, and ethylene/propylene copolymer, polyester resin represented by polyethylene terephthalate and polybutylene terephthalate, and polymethylacrylate, and polyvinyl chloride resin, as an organic resin coat or a polyester system, an urethane system, an epoxy system, acrylic, a fluorine system, and a melamine system, or two-layer. As for the above-mentioned coating, it is more desirable than the viewpoint of an environmental consideration that neither contains the rust preventive pigment of a chromium system.

[0021] The organic resin film which carried out the laminating of the biaxial-stretching polyethylene terephthalate by which shank printing was carried out to either of the polybutylene terephthalate films which are the colored polyvinyl chloride resin film, the polyolefin resin film, or polyester resin as an example of a two-layer organic resin coat using a heating laminating or adhesives, and was double-stratified can be mentioned. Moreover, it is not limited about organic resin coats other than these organic resin films, either, and is usable also about a fluororesin coat, a styrene resin coat, the coat that consists of acrylic Butadiene Styrene, and various rubber system coats.

[0022] The well-known laminating approach can be chosen as an approach of carrying out the laminating of these organic resin coats to the galvanized steel sheet in which the after-treatment coat was



made to form. For example, in the laminating of a thermoplastics film, after applying adhesives to the galvanized steel sheet which gave the after-treatment coat by the roll coater and passing desiccation oven, an adhesives spreading side is contacted in a thermoplastics film, and with the lamination roll of two which counters, both are inserted and are stuck by pressure. Subsequently, it considers as the makeup steel plate of this invention by [ which back-cool ] heating the steel plate which carried out the laminating of the film, having softened resin, having passed between the metal embossing roll and the rubber covered roll which counters, and having made the concavo-convex pattern form in a resin film front face. About adhesives, the adhesives suitable for an organic resin film can be chosen freely, and can be applied.

[0023] Moreover, when said organic resin coat is spreading film of a coating, a paint steel plate is manufactured by cooling the process which applies a coating by the roll coater with a conventional method, and passes desiccation oven, after repeating only the number of the spreading layers which carry out a laminating. Moreover, even if the organic resin coat in the front face and rear face of a makeup steel plate of this invention is the same and they differ, it does not interfere, if needed, it can choose suitably one sort of the aforementioned resin film and the coating spreading film, or two sorts or more, can combine them, and can apply them.

[0024] Moreover, it is necessary to call for electromagnetic wave shielding and weldability in the application of sheathing covering of an electrical machinery product etc., and for the after-treatment coat to have conductivity. In that case, only one side is used with the configuration of the galvanized steel sheet which has only an after-treatment coat, without carrying out the laminating of the organic resin coat. In this application, it is required for the surface electrical resistance (JIS K 7194) by the four point probe method of an after-treatment coat side to be 0.5ohms or less.

[0025] When it is applied to the application to which only this one side does not carry out the laminating of the organic resin coat and severe corrosion resistance is required especially, the coat containing vanadium is suitable for the after-treatment coat made to form after a galvanization. When fingerprint-proof nature is needed for an after-treatment coat at conductivity and coincidence, you may make it form the organic resin coat of a thin film with a thickness of less than 1 micrometer on an after-treatment coat further again in the range which does not spoil a surface-electrical-resistance value. As an organic resin coat of a thin film, common organic resin, such as acrylic, an urethane system, a polyester system, and an epoxy system, can be used.

[0026]

[Example] Hereafter, an example is shown and this invention is further explained to a detail.

(Examples 1-3) board thickness: -- 0.5mm cold rolled sheet steel -- a law -- electrolytic degreasing and after carrying out acid washing, the electrogalvanizing coat (one side: Zn:5 g/m<sup>2</sup>) was made to form in both sides of a steel plate according to the following conditions by the method

[The processing conditions of electrogalvanizing]

Plating bath composition Zinc sulfate : 250 g/L An ammonium sulfate : 30 g/L PH : 2.5 Bath temperature : 40 degrees C Current density : 20 A/dm<sup>2</sup> [0027] Then, cathode electrolysis processing was performed on condition that the following, and the after-treatment coat containing the vanadium of the thickness which changes the processing time and is shown in Table 1 was made to form.

[The processing conditions in which the after-treatment coat containing vanadium is made to form]

A processing liquid presentation Vanadium sulfate : 10 g/L Heavy ammonium phosphate : 5 g/L A sodium sulfate : 20 g/L An ammonium sulfate : 10 g/L Magnesium sulfate : 20 g/L PH : 3.0 Solution temperature : 45 degrees C Current density : 5 A/dm<sup>2</sup> [0028] Thus, the plating steel plate was heated to 200 degrees C after spreading so that a bar coating machine might be used and the thickness after desiccation might be set to 2 micrometers in the adhesives of an olefin / epoxy system, the adhesives spreading side was contacted in the non-extended polypropylene film (150 micrometers), using the rubber covered roll of a pair, it inserted, and the laminating was stuck by pressure and carried out to both sides of the obtained plating steel plate. Subsequently, as it touched, when a laminating steel plate was heated at 180 degrees C, and an embossing roll inserted into a polypropylene film and pressurized it using the embossing roll and rubber covered roll of a grain-like pattern, it considered as the makeup

steel plate which has a grain-like front face.

[0029] After making a galvanization coat form in the same cold rolled sheet steel as an example 1 like an example 1, (Example 4) The amount of coats after drying polyacrylic acid on the one side is 10 mg/m<sup>2</sup>. It is made to be the same as that of an example 1 except having applied in the bar coating machine so that it might become. The polypropylene film covering steel plate was created, subsequently embossing was performed to the polypropylene film plane like the example 1, and it considered as the makeup steel plate which has a grain-like front face.

[0030] (Example 5) board thickness: -- 0.5mm cold rolled sheet steel -- a law -- the makeup steel plate which consists of a polypropylene film covering steel plate which performed embossing to the front face like an example 4 was created except having made the composite coatings (one side: Zn:5g/m<sup>2</sup>, Co:25 mg/m<sup>2</sup>, Mo:7 mg/m<sup>2</sup>) which consist of zinc, cobalt, and molybdenum on condition that the following form by the method, after carrying out acid washing, electrolytic degreasing and.

[The processing conditions of composite coatings]

A bath presentation A zinc sulfate : 250 g/L Cobalt sulfate : 50 g/L Ammonium molybdate : 0.1 g/L An ammonium sulfate : 30 g/L PH : 3.0 Bath temperature : 40 degrees C Current density : 20 A/dm<sup>2</sup> [0031]

(Example 6) Adhesives created the makeup steel plate which consists of a polybutylene terephthalate film covering steel plate with which polyester system adhesives and a resin film performed embossing to the front face like [ except that whenever / stoving temperature / of the plate before a non-extended polybutylene terephthalate film (75 micrometers), a film laminating, and embossing / is 230 degrees C ] the example 5.

[0032] (Example 7) The makeup steel plate which consists of a two-layer resin film covering steel plate which performed embossing to the front face like an example 6 was created except being the film with which the resin film made two-layer the biaxial extension polyethylene terephthalate film (25 micrometers) and non-extended polybutylene terephthalate film (75 micrometers) by which shank printing was carried out using polyester system ink using urethane system adhesives.

[0033] (Example 8) Acrylic adhesives were used and the makeup steel plate which consists of an acrylic resin film covering steel plate which performed embossing to the front face like an example 5 was created except having used the acrylic film (80 micrometers) which consists of blend resin of 40 % of the weight of polymethylacrylates, and 60 % of the weight of methyl methacrylates / butyl acrylate copolymers.

[0034] (Example 9) Polyester system adhesives were used and the makeup steel plate which consists of a polyvinyl chloride resin film covering steel plate which performed embossing to the front face like an example 5 was created except having used the polyvinyl chloride film (150 micrometers).

[0035] (Example 10) The makeup steel plate which consists of a two-layer resin film covering steel plate was created like the example 9 except having used the film with which the biaxial-stretching polyethylene terephthalate film (25 micrometers) by which shank printing was carried out using polyester system ink, and the polyvinyl chloride film (150 micrometers) were made two-layer using urethane system adhesives.

[0036] (Example 11) The bar coating machine was used, and as the thickness of film after desiccation was set to 20 micrometers, it applied the heat-curing mold polyester system coating which does not contain the rust-proofer of a chromium system to one side of the plating steel plate created like the example 5. Then, the plating steel plate was heated at 200 degrees C, and the makeup steel plate which can be burned for 5 minutes and consists of a polyester system paint steel plate was created.

[0037] (Examples 12-14) The makeup steel plate which consists of a polypropylene covering steel plate was created like the example 1 except having made the after-treatment coat containing the cobalt of the thickness which carries out electrolysis processing on condition that the following, changes the processing time into the galvanized steel sheet created like the example 1, and is shown in Table 1 form.

[The processing conditions in which the after-treatment coat containing cobalt is made to form]

A liquid presentation Cobalt sulfate : 20 g/L Ammonium sulfate : 30 g/L PH : 3.0 Solution temperature : 45 degrees C Current density : 10 A/dm<sup>2</sup> [0038] (Example 15) The amount of coats after drying

polyacrylic acid on the one side, after creating a plating steel plate like an example 12 is 10mg/m<sup>2</sup>. The makeup steel plate which consists of a polypropylene covering steel plate was created like the example 10 except having applied in the bar coating machine so that it might become.

[0039] (Example 16) The makeup steel plate which consists of a polypropylene covering steel plate was created like the example 15 except having used the same composite-coatings steel plate as an example 5.

[0040] (Example 17) Adhesives created the makeup steel plate which consists of a polybutylene terephthalate film covering steel plate with which polyester system adhesives and a resin film performed embossing to the front face like [ except that whenever / stoving temperature / of the plate before a non-extended polybutylene terephthalate film (75 micrometers), a film laminating, and embossing / is 230 degrees C ] the example 16.

[0041] (Example 18) The makeup steel plate which consists of a two-layer resin film covering steel plate was created like the example 17 except being the film with which the resin film made two-layer the biaxial extension polyethylene terephthalate film (25 micrometers) and non-extended polybutylene terephthalate film (75 micrometers) by which shank printing was carried out using polyester system ink using urethane system adhesives.

[0042] (Example 19) The makeup steel plate which consists of an acrylic resin film covering steel plate like an example 16 was created except having used the acrylic film (80 micrometers) same as acrylic adhesives and a resin film as adhesives as an example 6.

[0043] (Example 20) Polyester system adhesives were used and the makeup steel plate which consists of a polyvinyl chloride resin film covering steel plate which performed embossing to the front face like an example 16 was created except having used the polyvinyl chloride film (150 micrometers).

[0044] (Example 21) The makeup steel plate which consists of a two-layer resin film covering steel plate was created like the example 20 except having used the film with which the biaxial-stretching polyethylene terephthalate film (25 micrometers) by which shank printing was carried out using polyester system ink, and the polyvinyl chloride film (150 micrometers) were made two-layer using urethane system adhesives.

[0045] (Example 22) The bar coating machine was used, and as the thickness of film after desiccation was set to 20 micrometers, it applied the heat-curing mold polyester system coating which does not contain the rust preventive pigment of a chromium system to the plating steel plate created like the example 16. Then, the plating steel plate was heated at 200 degrees C, and the makeup steel plate which can be burned for 5 minutes and consists of a polyester system paint steel plate was created.

[0046] (Examples 23-25) The after-treatment coat containing the vanadium of the amount of coats which carries out electrolysis processing like an example 1, changes the processing time into the galvanized steel sheet created like the example 1, and is shown in Table 1 was made to form. The laminating of the non-extended polypropylene film was carried out to one side of the obtained plating steel plate like the example 1. Subsequently, the embossing roll was used for the polypropylene film like the example 1, and it considered as the makeup steel plate which has a grain-like front face.

[0047] (Examples 26-28) The after-treatment coat containing the cobalt of the amount of coats which carries out electrolysis processing like an example 12, changes the processing time into the galvanized steel sheet created like the example 1, and is shown in Table 1 was made to form. The laminating of the non-extended polypropylene film was carried out to one side of the obtained plating steel plate like the example 1. Subsequently, the embossing roll was used for the polypropylene film like the example 1, and it considered as the makeup steel plate which has a grain-like front face.

[0048] (Example 1 of a comparison) Without making an after-treatment coat form, after making a galvanization coat form in the same steel plate as an example 1 like an example 1, the laminating of the same polypropylene film as the direct example 1 was carried out to the one side like the example 1, and the polypropylene film covering steel plate was created.

[0049] (Example 2 of a comparison) It is a chromic-acid bath (chromic anhydride: by carrying out cathode electrolysis using 25 g/L and sulfuric-acid:0.1 g/L) as after treatment after making a galvanization coat form in the same steel plate as an example 1 like an example 1. The polypropylene

film covering steel plate was created like the example 1 except having made the after-treatment coat which becomes one side from 40mg/the chromium hydration oxide of m<sup>2</sup> as chromium form.

[0050] (Example 3 of a comparison) Electrolysis processing was carried out like the example 1, and the after-treatment coat containing the vanadium of the amount of coats shown in Table 1 was made to form in the galvanized steel sheet created like the example 1. The laminating of the non-extended polypropylene film was carried out to one side of the obtained plating steel plate like the example 1, and the polypropylene film covering steel plate was created.

[0051] (Example 4 of a comparison) Electrolysis processing was carried out like the example 12, and the after-treatment coat containing the cobalt of the amount of coats shown in Table 1 was made to form in the galvanized steel sheet created like the example 1. The laminating of the non-extended polypropylene film was carried out to one side of the obtained plating steel plate like the example 1, and the polypropylene film covering steel plate was created.

[0052] The following property was evaluated about the makeup steel plate of the examples 1-28 acquired as mentioned above, and the polypropylene film covering steel plate of the examples 1-4 of a comparison.

(Adhesion of an organic resin coat) The adhesion of an organic resin coat of an organic resin coat covering steel plate was evaluated using the Erichsen test of the JIS K 6744 publication used for evaluation of the adhesion of polyvinyl chloride cladding. Slitting of two main tracks with spacing of 2.5mm was put in so that slitting which reaches the steel plate of 50mm die length in two main tracks with spacing of 2.5mm from the front face of an organic resin coat covering steel plate might be put in and it might intersect perpendicularly with the two main tracks further using a cutter. Then, 6mm overhang processing was performed using the Erichsen tester, and visual evaluation of exfoliation extent of an organic resin coat was carried out on the following criteria. About some organic resin coat covering steel plates used for evaluation, the piece of a stretch forming test was further immersed in the boiling water for 2 hours, and visual evaluation of exfoliation extent of an organic resin coat was carried out on the following criteria.

Fitness: Coat exfoliation is not accepted.

Defect: Coat exfoliation is accepted.

[0053] (Corrosion resistance of a double-sided organic resin coat covering steel plate) The organic resin coat covering steel plate of examples 1-22 and the examples 1 and 2 of a comparison was cut down in 50mmx100mm magnitude, the seal of the cutting plane was carried out with the vinyl tape, and it considered as the test piece. The salt spray test of 1000 hours was presented with this test piece based on JIS Z 2731. Visual evaluation of the generating situation of the rust of the organic resin coat side of the center section of the test piece after a trial was carried out on the following criteria.

Fitness: Generating of rust is not accepted.

Defect: Generating of rust (rust or white rust) is accepted.

[0054] (Corrosion resistance of the non-resin covering surface of an one side organic resin coat covering steel plate) The organic resin coat covering steel plate of examples 23-28 and the examples 3 and 4 of a comparison was cut down in 50mmx100mm magnitude, the seal of the cutting plane was carried out with the vinyl tape, and it considered as the test piece. The salt spray test of 12 hours was presented with this test piece based on JIS Z 2731. Visual evaluation of the generating situation of the rust of the non-resin coat side of the center section of the test piece after a trial was carried out on the following criteria.

Fitness: Generating of rust is not accepted.

Defect: Generating of rust (rust or white rust) is accepted.

[0055] (Conductivity of the non-resin covering surface of an one side organic resin coat covering steel plate) Using the low resistivity meter (the Mitsubishi Chemical make, form: RORESUTA GP MCP-T600), the surface-electrical-resistance value of the non-resin covering surface of the organic resin coat covering steel plate of examples 23-28 and the examples 3 and 4 of a comparison was measured by the 4 probe contact resistance method according to JIS K 7194, and the following criteria estimated it.

O : <=0.5ohm and a x:>0.5-ohm evaluation result are shown in Tables 1 and 2. In addition, in the after-

treatment coat of Table 1, a class shows that V and P are contained in a coat by V/P, Co shows that Co is contained in a coat, and Cr shows that Cr is contained in a coat. About the amount of after-treatment coats, V shows that 130mg/m<sup>2</sup>, and P are contained 40 mg/m<sup>2</sup> to an after-treatment coat in the example 1, for example. furthermore -- the organic resin coat of Table 1 -- PP -- a polypropylene film -- in PBT, PET shows a polyethylene terephthalate film and PVC shows a polyvinyl chloride film for a polybutylene terephthalate film. In the examples 7 and 18, the upper layer is [ a lower layer ] the two-layer film of PBT in PET, and the upper layer shows that a lower layer is the two-layer film of PVC in PET in examples 10 and 21.

[0056]

[Table 1]

実施例 または 比較例	亜鉛めっき皮膜 (mg/m <sup>2</sup> )			後処理皮膜		ポリタリ 酸の皮 膜量 (mg/m <sup>2</sup> )	有機樹脂皮膜	
	Zn	Co	Mo	種 類	皮膜量 (mg/m <sup>2</sup> )		種 類	厚 さ (μm)
実施例 1	5000	—	—	V/P	130/40	—	PP	150
実施例 2	5000	—	—	V/P	5/3	—	PP	150
実施例 3	5000	—	—	V/P	450/50	—	PP	150
実施例 4	5000	—	—	V/P	130/40	10	PP	150
実施例 5	5000	25	7	V/P	130/40	10	PP	150
実施例 6	5000	25	7	V/P	130/40	10	PBT	75
実施例 7	5000	25	7	V/P	130/40	10	PET/PBT	25/75
実施例 8	5000	25	7	V/P	130/40	10	ポリ イミド	80
実施例 9	5000	25	7	V/P	130/40	10	PVC	150
実施例 10	5000	25	7	V/P	130/40	10	PET/PVC	25/150
実施例 11	5000	25	7	V/P	130/40	10	ポリエステル塗料	20
実施例 12	5000	—	—	Co	200	—	PP	150
実施例 13	5000	—	—	Co	5	—	PP	150
実施例 14	5000	—	—	Co	400	—	PP	150
実施例 15	5000	—	—	Co	200	10	PP	150
実施例 16	5000	25	7	Co	200	10	PP	150
実施例 17	5000	25	7	Co	200	10	PBT	75
実施例 18	5000	25	7	Co	200	10	PET/PBT	25/75
実施例 19	5000	25	7	Co	200	10	ポリ イミド	80
実施例 20	5000	25	7	Co	200	10	PVC	150
実施例 21	5000	25	7	Co	200	10	PET/PVC	25/150
実施例 22	5000	25	7	Co	200	10	ポリエステル塗料	20
実施例 23	5000	—	—	V/P	5/5	—	PP(片面)	150
実施例 24	5000	—	—	V/P	100/20	—	PP(片面)	150
実施例 25	5000	—	—	V/P	150/50	—	PP(片面)	150
実施例 26	5000	—	—	Co	10	—	PP(片面)	150
実施例 27	5000	—	—	Co	80	—	PP(片面)	150
実施例 28	5000	—	—	Co	200	—	PP(片面)	150
比較例 1	5000	—	—	—	—	—	PP	150
比較例 2	5000	—	—	Cr	40	—	PP	150
比較例 3	5000	—	—	V/P	250/80	—	PP(片面)	150
比較例 4	5000	—	—	Co	430	—	PP(片面)	150

[0057]

[Table 2]

実施例 または 比較例	樹脂皮膜密着性		耐 食 性		導 電 性
	6mm張出	沸騰水浸漬	樹脂被覆面	後処理皮膜面	後処理皮膜面
実施例 1	良 好	良 好	良 好	—	—
実施例 2	良 好	良 好	良 好	—	—
実施例 3	良 好	良 好	良 好	—	—
実施例 4	良 好	良 好	良 好	—	—
実施例 5	良 好	良 好	良 好	—	—
実施例 6	良 好	良 好	良 好	—	—
実施例 7	良 好	良 好	良 好	—	—
実施例 8	良 好	良 好	良 好	—	—
実施例 9	良 好	良 好	良 好	—	—
実施例 10	良 好	良 好	良 好	—	—
実施例 11	良 好	良 好	良 好	—	—
実施例 12	良 好	良 好	良 好	—	—
実施例 13	良 好	良 好	良 好	—	—
実施例 14	良 好	良 好	良 好	—	—
実施例 15	良 好	良 好	良 好	—	—
実施例 16	良 好	良 好	良 好	—	—
実施例 17	良 好	良 好	良 好	—	—
実施例 18	良 好	良 好	良 好	—	—
実施例 19	良 好	良 好	良 好	—	—
実施例 20	良 好	良 好	良 好	—	—
実施例 21	良 好	良 好	良 好	—	—
実施例 22	良 好	良 好	良 好	—	—
実施例 23	良 好	良 好	—	良 好	○
実施例 24	良 好	良 好	—	良 好	○
実施例 25	良 好	良 好	—	良 好	○
実施例 26	良 好	良 好	—	良 好	○
実施例 27	良 好	良 好	—	良 好	○
実施例 28	良 好	良 好	—	良 好	○
比較例 1	不 良	不 良	不 良	—	—
比較例 2	良 好	良 好	良 好	—	—
比較例 3	良 好	良 好	—	良 好	×
比較例 4	良 好	良 好	—	良 好	×

[0058] As shown in Table 1 and 2, the makeup steel plate of this invention which comes to carry out the laminating of the organic resin coat to the plating steel plate in which the after-treatment coat which does not contain chromium was made to form shows the adhesion of the organic resin coat more than the resin coat covering steel plate using the plating steel plate in which the after-treatment coat containing conventional chromium was made to form, and an EQC, and corrosion resistance.

[0059]

[Effect of the Invention] The after-treatment coat to which this invention contains cobalt in a galvanization coat and its upper layer to both sides of a steel plate is formed. At least on or one side of the plating steel plate with which the polyacrylic acid spreading coat was further formed in the upper layer One film of polyolefin resin, polyester resin, acrylic resin, and polyvinyl chloride resin, Or it is the makeup steel plate which comes to carry out the laminating of the organic resin coat which is coating spreading film. It has the adhesion of the tree covering steel plate in which the after-treatment coat containing conventional chromium was made to form, and the organic resin coat more than an EQC, and corrosion resistance, and in order to make an after-treatment coat form without using chromium, there is

no possibility that the work environment at the time of manufacturing and the operating environment after manufacture may be polluted by harmful chromium.

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[Translation done.]